Physics of Electronics:

2. The Electronic Structure of Atoms (cont.)

July – December 2008

Contents overview

- Interpretation of wave function
- Uncertainty principle
- Beams of particles and potential barriers
- A particle in a 1D potential well
- The hydrogen atom
- The exclusion principle

Interpretation of the Wave Function

- Born interpretation:
  - The probability of finding the particle in the space volume d*V*, at the time *t*, is given by:

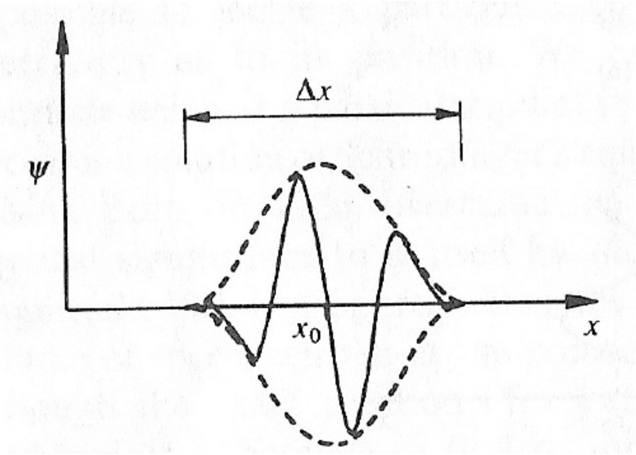
$$|\psi(x, y, z, t)|^2 dV \Rightarrow \int_{\text{whole space}} |\psi(x, y, z, t)|^2 dV = 1$$

(normalization)

- $\psi(x, t)$ also has to be:
  - Continuous and single valued on *x*.
  - Idem with its spatial first derivatives.

Heisenberg Principle

- A rigorous demonstration using matrix mechanics



$$\boxed{\Delta p \, \Delta x \geqslant \hbar/2}$$

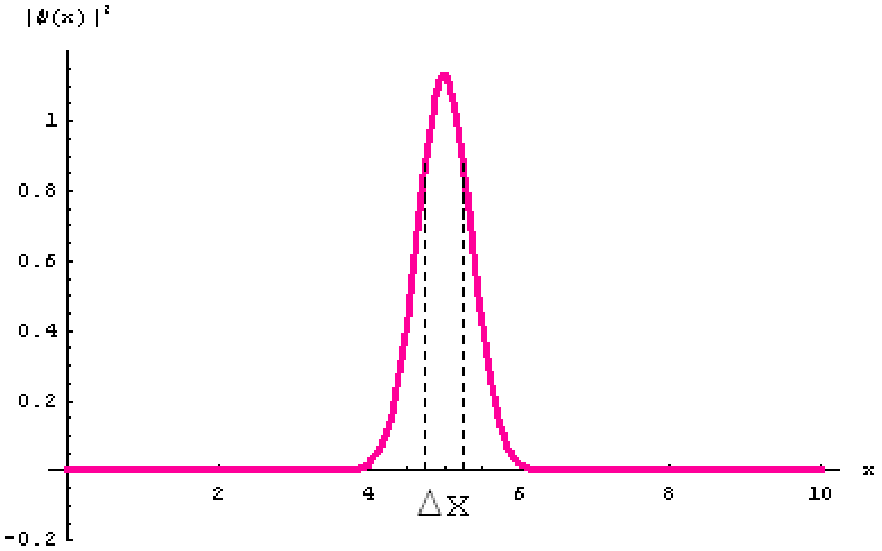
- In QM there are pair of physical quantities (called conjugates) for which this relation holds, e.g.:

$$\boxed{\Delta E \, \Delta t \geqslant h}$$

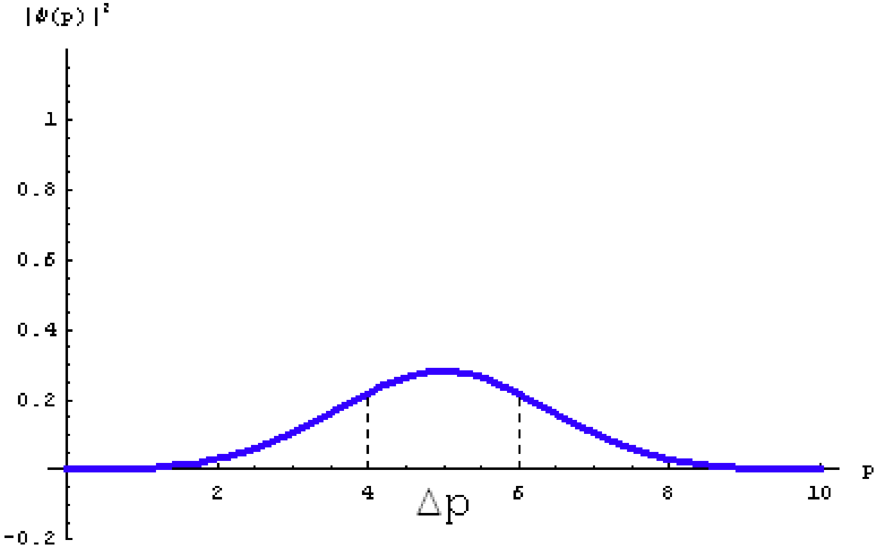
For an experimental demo: *Nature* **371**, 594 - 595 (13 October 2002)

Heisenberg Principle

- What does exactly Δq mean?

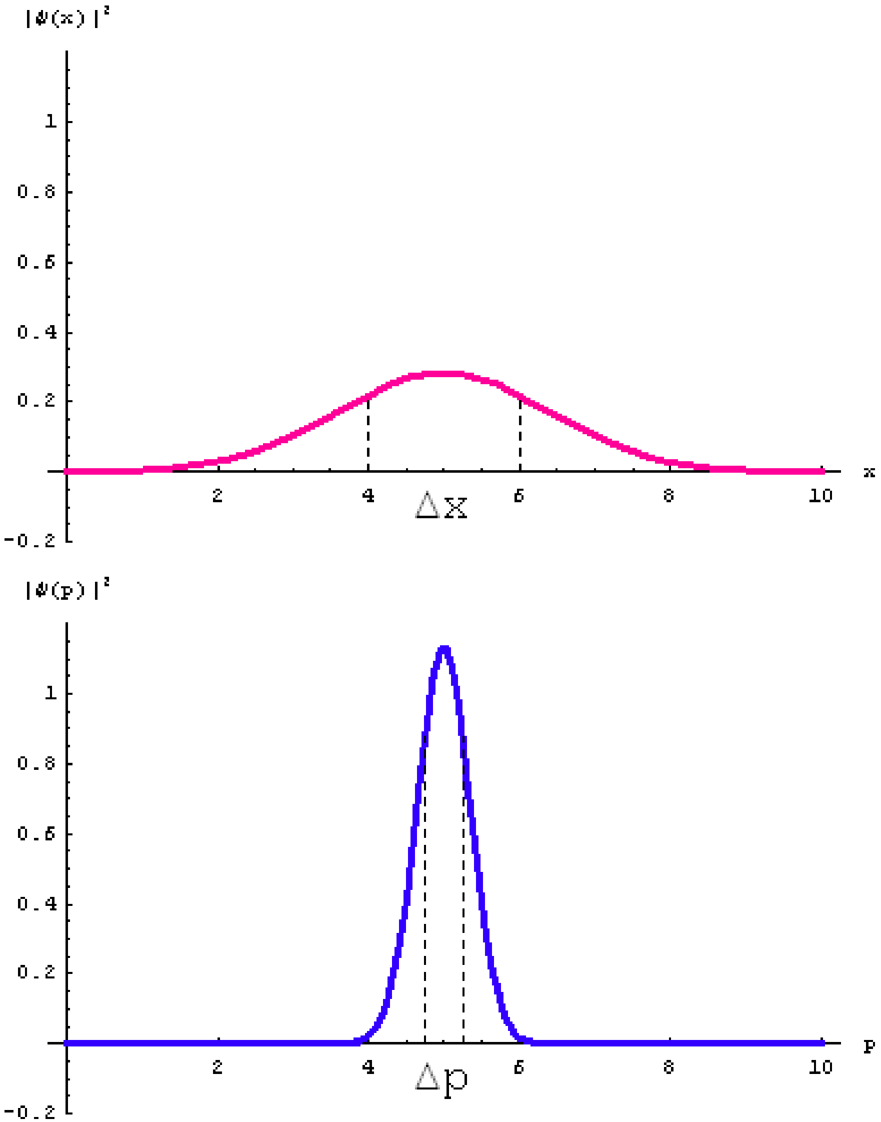


Δq is the standard deviation of the probability density



Heisenberg Principle

- What does exactly Δq mean?

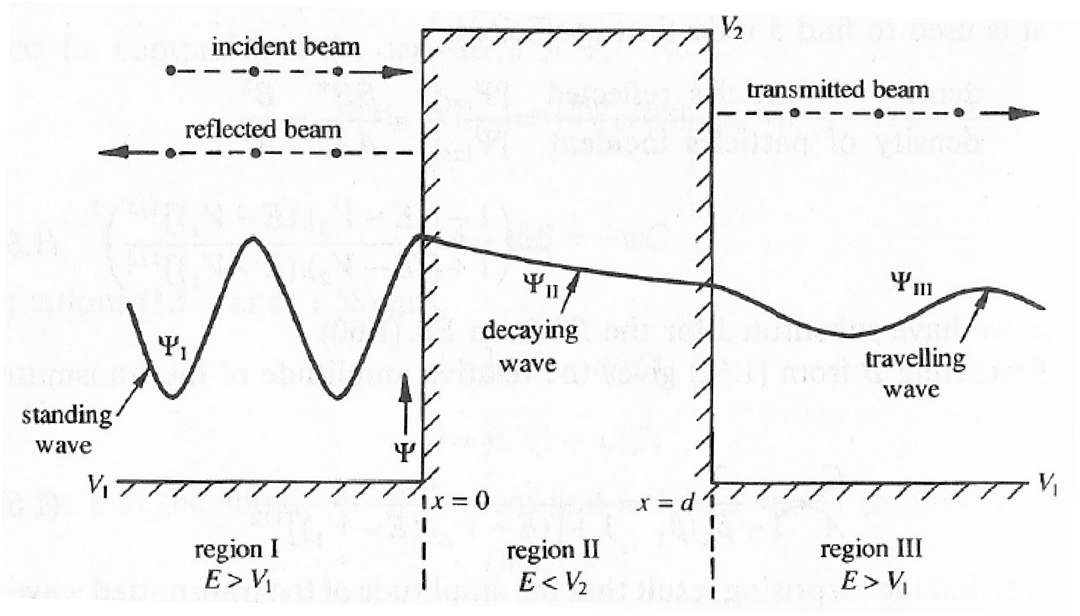


Δq is the standard deviation of the probability density

The Heisenberg principle applies to quantites whose standard deviation are not independent. It happens when those quantites are FT related.

Potential Barriers

- Narrow potential barrier ($V_1 < E < V_2$):



SE is written for every region, from which:

$$\Psi_I = A\exp(\mathrm{j}\beta x) + B\exp(-\mathrm{j}\beta x)$$
$$\Psi_{II} = C\exp(-\alpha x) + D\exp(\alpha x)$$
$$\Psi_{III} = F\exp(\mathrm{j}\beta x)$$

where $$\alpha^2 = \frac{2m}{\hbar^2}(V_2 - E)$$

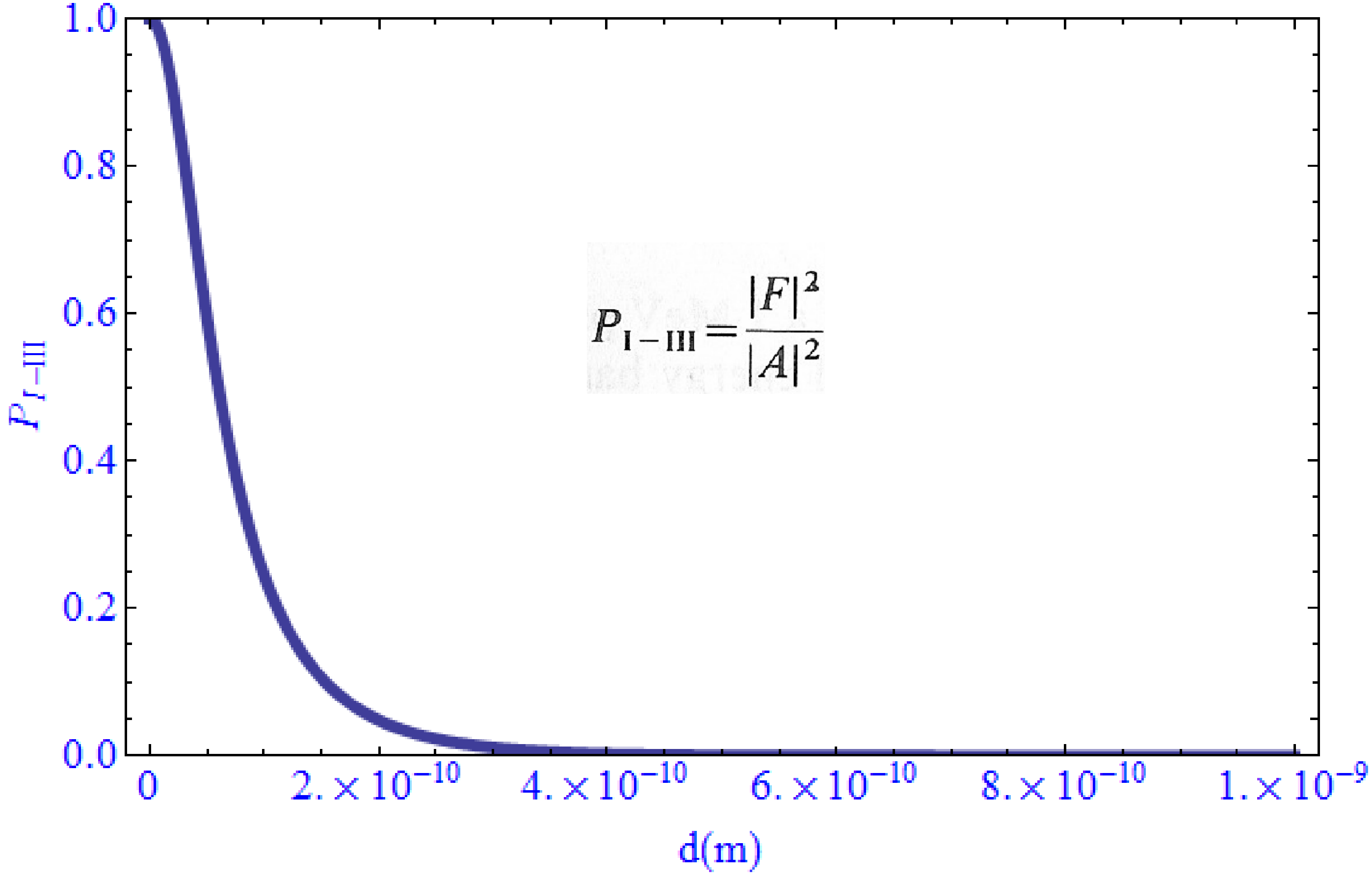
$$\beta^2 = \frac{2m}{\hbar^2}(E - V_1)$$

Constants *A*, *B*, *C*, *D*, *F* are obtained from continuity and normalization. In particular:

$$F = A\exp(-\mathrm{j}\beta d)[\cosh(\alpha d) + \tfrac{1}{2}(\alpha/\beta - \beta/\alpha)\sinh(\alpha d)]^{-1}$$

Potential Barriers

- Narrow potential barrier ($V_1 < E < V_2$):
  - Transmission from I to III



As comparison, Bohr radius = 0.05 nm

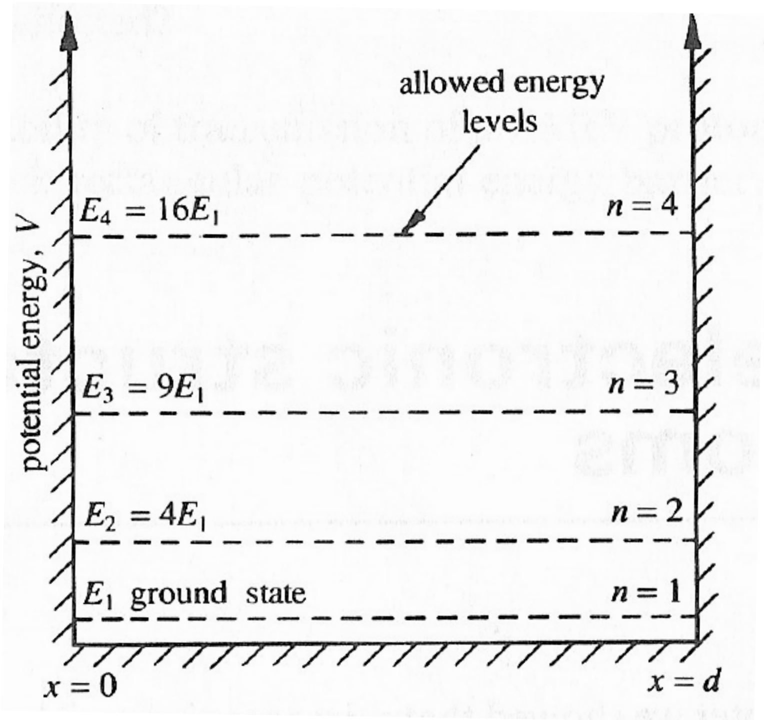
A Particle in a 1D Potential Well

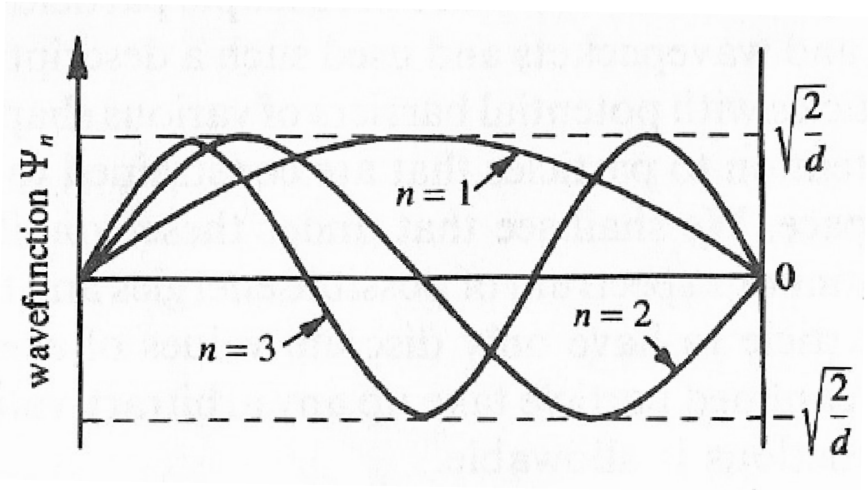
- Infinite well:

$$\beta^2 = (2m/\hbar^2)E$$

$$V = \begin{cases} 0 \text{ for } 0 < x < d \\ \infty \text{ elsewhere} \end{cases} \xrightarrow{\text{SE}} \frac{d^2\Psi}{dx^2} + \frac{2m}{\hbar^2}E\Psi = 0 \longrightarrow \Psi = Ae^{j\beta x} + Be^{-j\beta x}$$

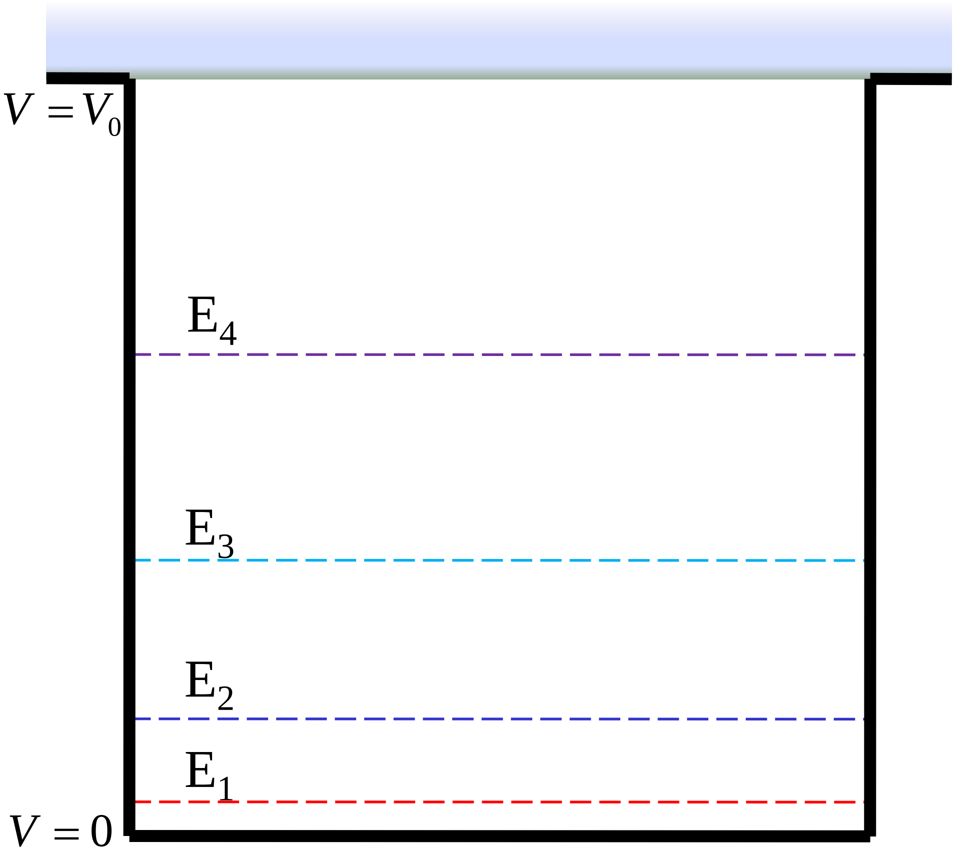
$$\longrightarrow \quad \Psi = (2/d)^{1/2}\sin(n\pi x/d) \qquad E = \frac{\hbar^2 n^2 \pi^2}{2md^2} = \frac{n^2h^2}{8md^2} \qquad n = 1,2,3,\ldots$$

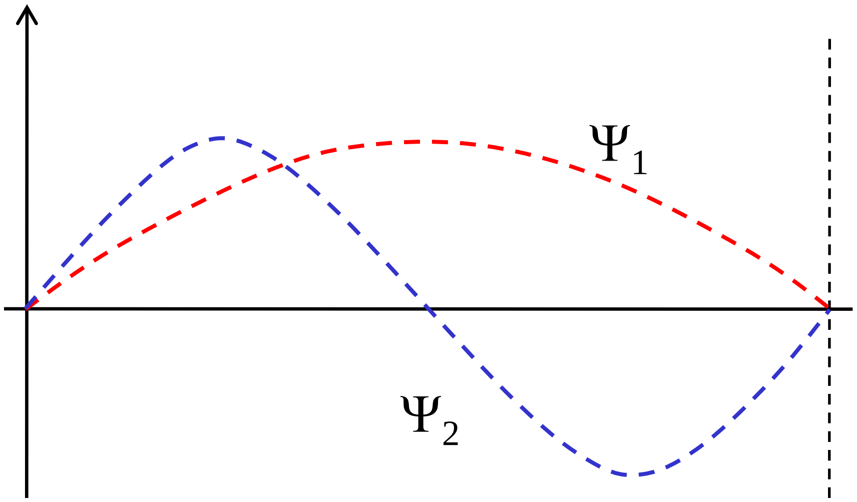




A Particle in a 1D Potential Well

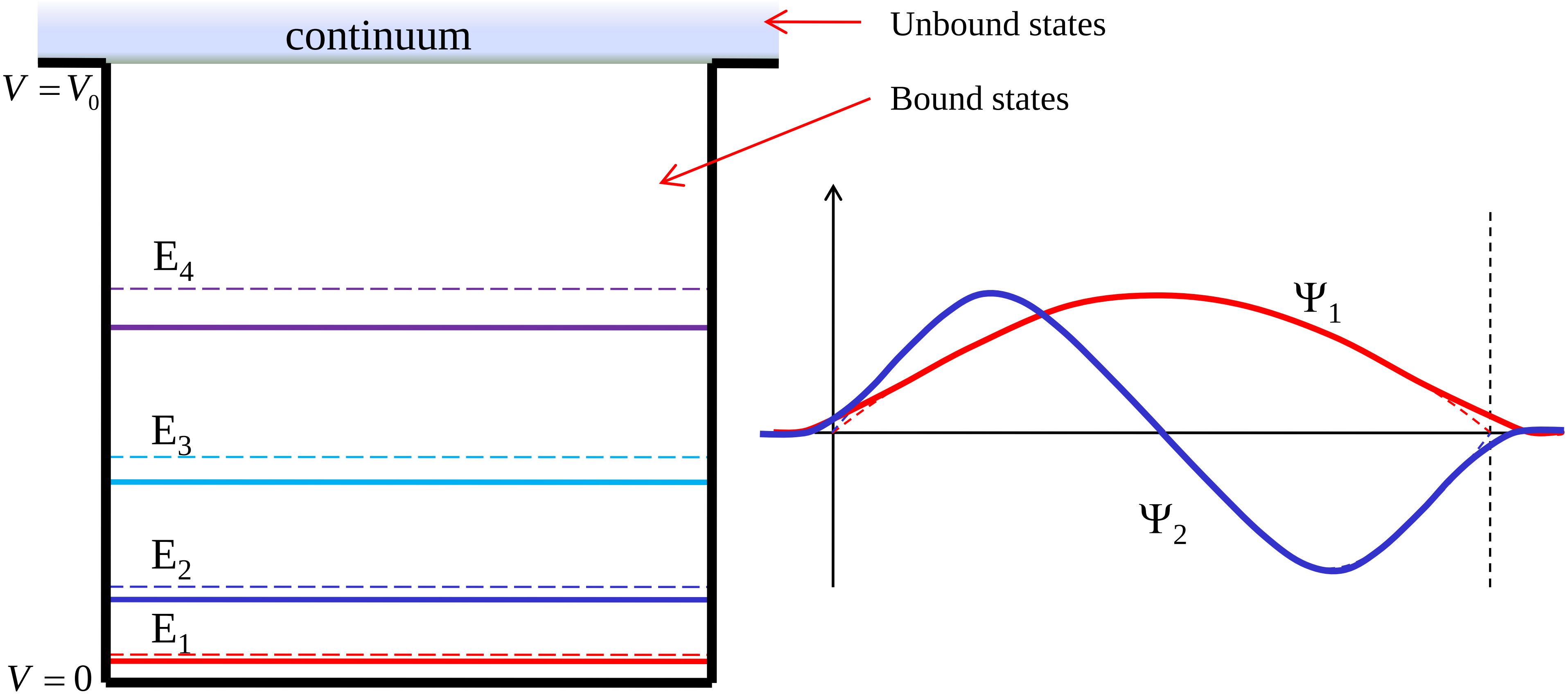
- Finite well:





A Particle in a 1D Potential Well

- Finite well (left as excercise):



Unbound states

Bound states

The Hydrogen Atom

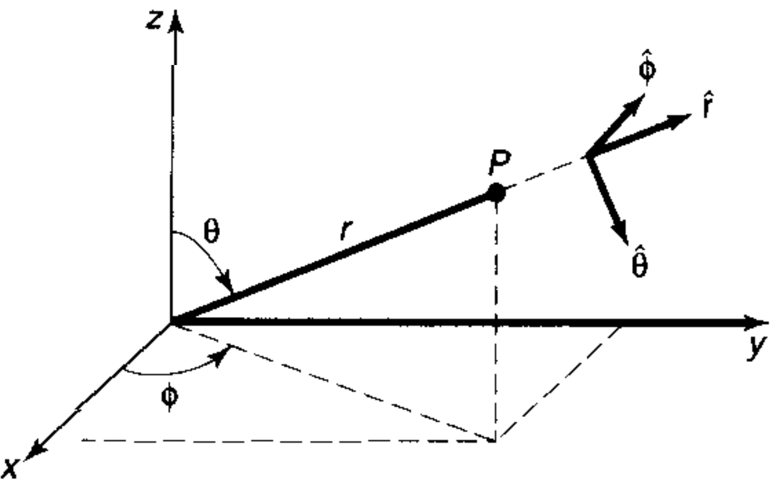
- Electron moving in the electric field of the nucleus:

$$V = -e^2/(4\pi\epsilon_0 r)$$

  - We have to solve the time-independent SE:

$$\nabla^2\Psi + \frac{2m}{\hbar^2}(E - V)\Psi = 0$$

  - Given the symmetry, we use it in polar coordinates:



$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right) + \frac{1}{r^2}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Psi}{\partial\theta}\right)$$

$$+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\Psi}{\partial\phi^2} + \frac{2m}{\hbar^2}(E - V)\Psi = 0$$

The Hydrogen Atom

- Electron moving in the electric field of the nucleus:

$$V = -e^2/(4\pi\epsilon_0 r)$$

  - Full solution by separation of variables assuming:

$$\Psi(r, \theta, \phi) = R(r)\underbrace{\Theta(\theta)\Phi(\phi)}_{Y(\theta,\, \phi)}$$

  - Some algebra (and convenient election of constants) gives:

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}[V(r) - E] = l(l+1);$$

$$\left.\begin{array}{c} \dfrac{1}{\Theta}\left[\sin\theta\dfrac{d}{d\theta}\left(\sin\theta\dfrac{d\Theta}{d\theta}\right)\right] + l(l+1)\sin^2\theta = m^2; \\ \dfrac{1}{\Phi}\dfrac{d^2\Phi}{d\phi^2} = -m^2. \end{array}\right\} \text{Independent of } V$$

The Hydrogen Atom

- Electron moving in the electric field of the nucleus:

$$V = -e^2/(4\pi\epsilon_0 r)$$

  - Azimuth angle part:

$$\frac{d^2\Phi}{d\phi^2} = -m^2\Phi \Rightarrow \Phi(\phi) = e^{im\phi}. \quad \text{but} \quad \Phi(\phi + 2\pi) = \Phi(\phi). \Longrightarrow \quad m = 0, \pm 1, \pm 2, \ldots.$$

  - Polar angle part:

$$\frac{1}{\Theta}\left[\sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right)\right] + l(l+1)\sin^2\theta = m^2; \quad \Longrightarrow \quad \Theta(\theta) = A P_l^m(\cos\theta),$$

where:

$$P_l^m(x) \equiv (1 - x^2)^{|m|/2}\left(\frac{d}{dx}\right)^{|m|} P_l(x), \Longrightarrow |m| \le l \Longrightarrow m = -l, -l+1, \ldots, -1, 0, 1, \ldots, l-1, l.$$

$$P_l(x) \equiv \frac{1}{2^l l!}\left(\frac{d}{dx}\right)^l (x^2 - 1)^l. \Longrightarrow \quad l = 0, 1, 2, \ldots$$

The Hydrogen Atom

- Electron moving in the electric field of the nucleus:

$$V = -e^2/(4\pi\epsilon_0 r)$$

  - (Total) angular part depends on two integer numbers:

$$Y(\theta, \phi) = \Theta(\theta)\Phi(\phi) = Y_l^m(\theta, \phi)$$

  - After normalization (R and Y are normalized independently):

$$Y_l^m(\theta, \phi) = \epsilon\sqrt{\frac{(2l+1)}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}\, e^{im\phi}\, P_l^m(\cos\theta),$$

where $\epsilon = (-1)^m$ for $m \geq 0$ and $\epsilon = 1$ for $m \leq 0$.

The Hydrogen Atom

- Electron moving in the electric field of the nucleus:

$$V = -e^2/(4\pi\epsilon_0 r)$$

  - Radial part

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}[V(r) - E] = l(l+1);$$

whose solution is (see any book on Q.M.):

$$R_{nl}(r) = \frac{1}{r}\rho^{l+1}e^{-\rho}v(\rho), \quad \text{with} \quad \rho = \frac{r}{an}. \quad (a \text{ is the Bohr radius})$$

where:

$$\left.\begin{aligned} v(\rho) &= L^{2l+1}_{n-l-1}(2\rho), \\ L^{p}_{q-p}(x) &\equiv (-1)^p\left(\frac{d}{dx}\right)^p L_q(x) \\ L_q(x) &\equiv e^x\left(\frac{d}{dx}\right)^q\left(e^{-x}x^q\right) \end{aligned}\right\} \Rightarrow \quad l = 0, 1, 2, \ldots, n-1.$$

The Hydrogen Atom

- Electron moving in the electric field of the nucleus:

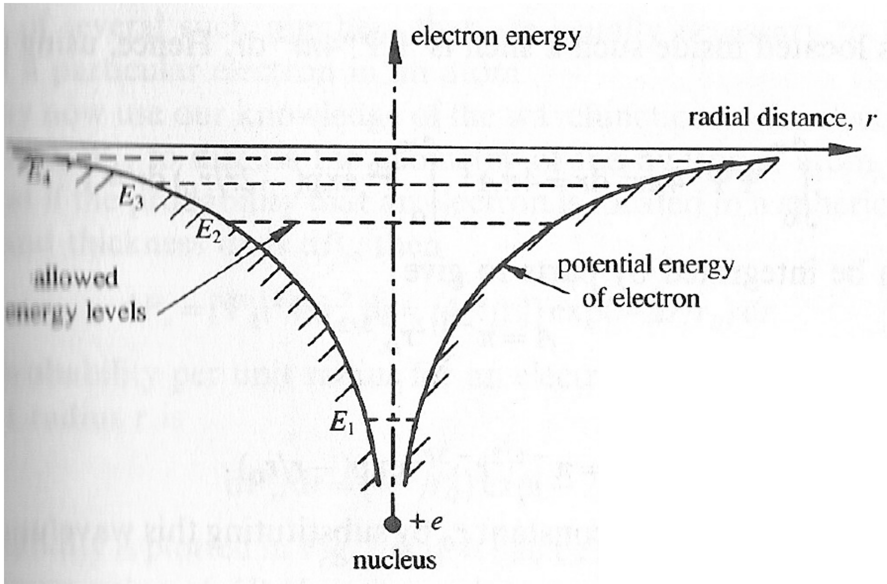
$$V = -e^2/(4\pi\epsilon_0 r)$$

  - Radial part

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}[V(r) - E] = l(l+1);$$

whose solution is (see any book on Q.M.):

$$E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2} = \frac{E_1}{n^2}, \quad n = 1, 2, 3, \ldots .$$



The Hydrogen Atom

- Electron moving in the electric field of the nucleus:

$$V = -e^2/(4\pi\epsilon_0 r)$$

  - Total solution:

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)\, Y_l^m(\theta, \phi),$$

  - After normalization:

$$\psi_{nlm} = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}}\, e^{-r/na} \left(\frac{2r}{na}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right) Y_l^m(\theta, \phi).$$

  - Notice that the w.f. depends on 3 integers (or quantum numbers) but the energy only in one of them. I.e. several w.f.'s can have the same value of energy. This is called DEGENERACY.

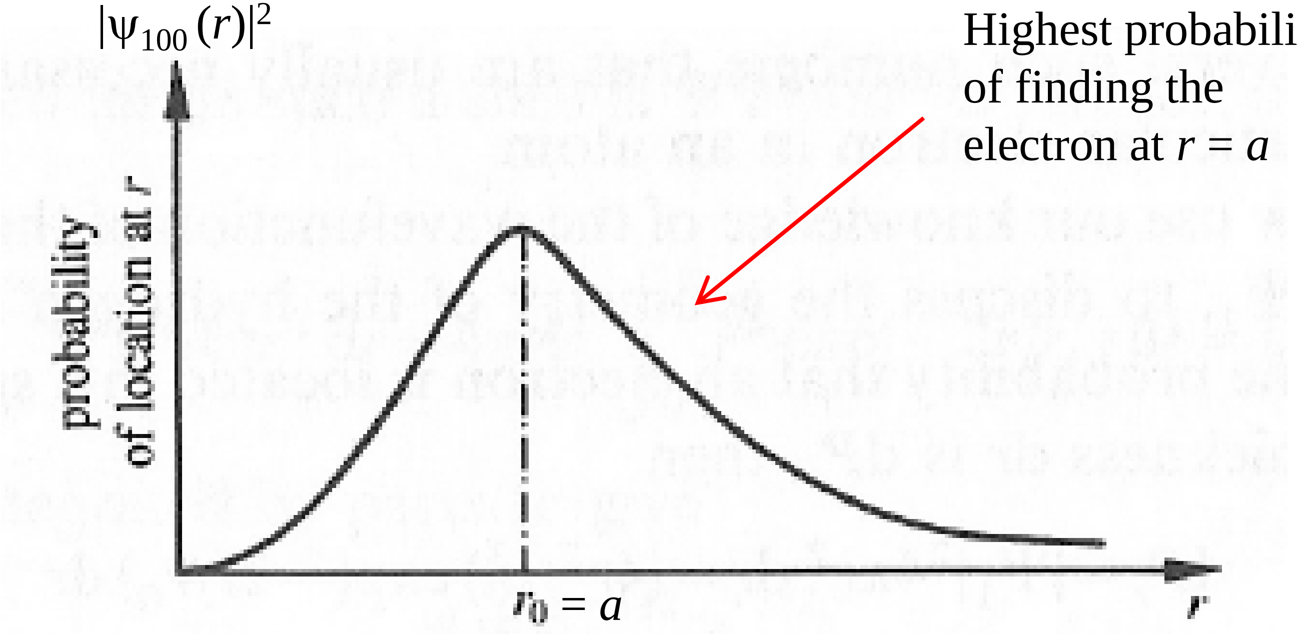
The Hydrogen Atom

- Electron moving in the electric field of the nucleus:

$$V = -e^2/(4\pi\epsilon_0 r)$$

  - The ground state (level with lowest energy) is:

$$\psi_{100}(r,\theta,\phi) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}.$$



Highest probability of finding the electron at $r = a$

Spin & Exclusion Principle

- It exist another quantum number describing the electron in an atom: SPIN number. It represents the rotation of the electron over its own axis. It can be obtained by solving the relativistic SE.
- Therefore, an electron inan atom is completely specified by 4 quantum numbers:

$$(n, l, m, s).$$

- The exclusion principle says that no 2 electrons can have the same quantum numbers.

Exclusion Principle

- This applies for any atom, which permits to construct the following table:

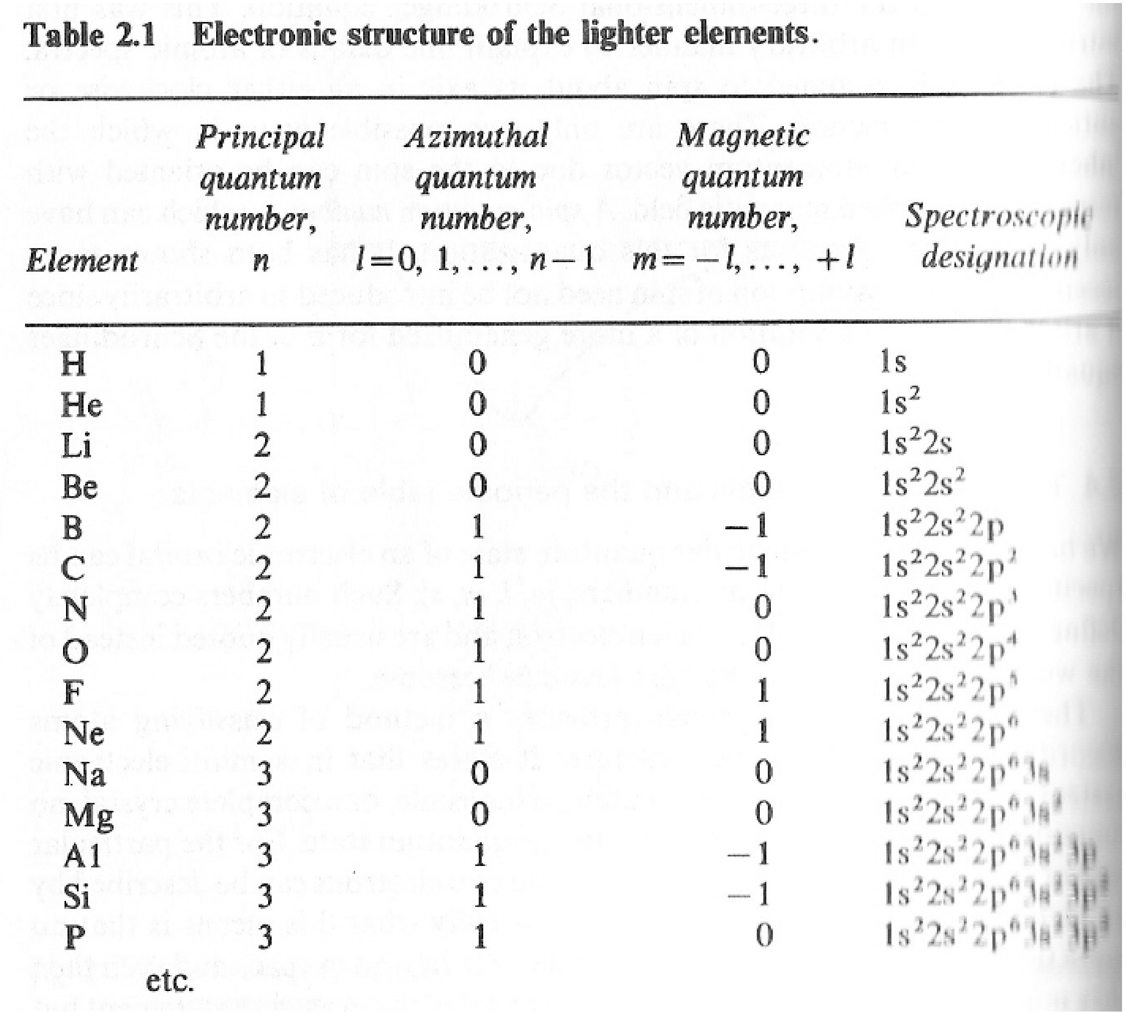
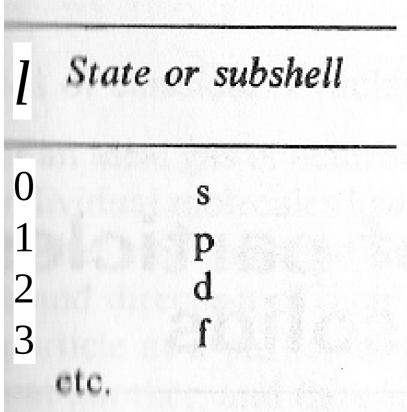


Table 2.1 Electronic structure of the lighter elements.

Element	*Principal quantum number,* n	*Azimuthal quantum number,* $l = 0, 1, \ldots, n-1$	*Magnetic quantum number,* $m = -l, \ldots, +l$	*Spectroscopic designation*
H	1	0	0	$1s$
He	1	0	0	$1s^2$
Li	2	0	0	$1s^2 2s$
Be	2	0	0	$1s^2 2s^2$
B	2	1	−1	$1s^2 2s^2 2p$
C	2	1	−1	$1s^2 2s^2 2p^2$
N	2	1	0	$1s^2 2s^2 2p^3$
O	2	1	0	$1s^2 2s^2 2p^4$
F	2	1	1	$1s^2 2s^2 2p^5$
Ne	2	1	1	$1s^2 2s^2 2p^6$
Na	3	0	0	$1s^2 2s^2 2p^6 3s$
Mg	3	0	0	$1s^2 2s^2 2p^6 3s^2$
Al	3	1	−1	$1s^2 2s^2 2p^6 3s^2 3p$
Si	3	1	−1	$1s^2 2s^2 2p^6 3s^2 3p^2$
P	3	1	0	$1s^2 2s^2 2p^6 3s^2 3p^3$

etc.

where:



l	*State or subshell*
0	s
1	p
2	d
3	f

etc.

Conclusions

- We have made a model of the atom:
  - One approximated (well)
  - One more realistic (hydrogen atom).
- The solution of the H atom gave rise to 3 quantum numbers.
- The complete description of an electronic state requires an extra number: spin.
- Exclusion principle. The set of 4 quantum numbers has to be different for every electron in an atom.